



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B23K 35/14, 35/26, H05K 3/34 // B23K 101/42	A1	(11) International Publication Number: WO 00/48784 (43) International Publication Date: 24 August 2000 (24.08.00)
(21) International Application Number: PCT/GB00/00533 (22) International Filing Date: 16 February 2000 (16.02.00) (30) Priority Data: 9903552.9 16 February 1999 (16.02.99) GB (71) Applicant (for all designated States except US): MULTICORE SOLDER S LIMITED [GB/GB]; Kelsey House, Wood Lane End, Hemel Hempstead, Herts HP2 4RQ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): STEEN, Hector, Andrew, Hamilton [GB/GB]; 211 Ebbens Road, Hemel Hempstead, Herts HP3 9RD (GB). (74) Agent: SILVERMAN, Warren; Haseline Lake & Co, Imperial House, 15-19 Kingsway, London WC2B 6UD (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LEAD-FREE SOLDER ALLOY POWDER PASTE USE IN PCB PRODUCTION		
(57) Abstract Tombstoning susceptibility and reflow peak temperature reduction of solder alloys, in particularly lead-free solder alloys, has been found to be achieved effectively by mixing the solder alloy in the form of an alloy paste with a low melting alloy utilised in powder form, in particular a Bi-containing alloy.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NK	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

LEAD-FREE SOLDER ALLOY POWDER PASTE USE IN PCB
PRODUCTION

5 This invention relates to lead-free solder alloy
powder usage in pastes for soldering components to
printed circuit boards (PCB's).

10 When lead-free solders are used in the soldering
of components to printed circuit boards, problems stem
from the increase in reflow (soldering) temperature
required by the main lead-free alternatives relative to
the eutectic Sn(PbAg) solders currently used. The
principal lead-free solders are based on the tin-
copper, tin-silver and tin-silver-copper eutectics,
15 melting at 227°C, 221°C and 217°C, respectively. These
alloys require relatively high reflow temperatures in
the range 230-240°C to obtain adequate soldering.
Reflow temperatures in this range may damage
temperature sensitive components. Thus, lead free
20 solders have not yet found widespread adoption in
electronics assembly despite their obvious advantages.

25 In order to lower lead-free alloy melting points
below 217°C, it is possible to alloy the above
mentioned lead-free solders with limited amounts of
bismuth, generally up to about 10%, typically 2-5% by
weight. There is indeed an additional advantage in
using bismuth in solid solution in tin in lead-free
alloys in that the bismuth has been found to strengthen
30 the lead-free alloys. The addition of bismuth has,
however, the disadvantage of introducing a melting
range. Thermal strains developing in an assembly on
cooling, in conjunction with solder joints with a
freezing range can, in unfavourable circumstances, lead
35 to hot cracking. This phenomenon of hot cracking has
been observed particularly in plated-through-hole

applications but not in surface mount reflow soldering, so bismuth containing alloys are viable in many solder paste applications.

5 A defect commonly found on reflow soldered printed circuit boards is that when chip components solder faster at one end than another and as a consequence are pulled by surface tension, they stand vertically on one pad, creating an electrical discontinuity. It is for
10 this reason that this behaviour is known as tombstoning. In current practice this is addressed by using a solder alloy with a melting range, but, where lead-free solders are concerned, no solution has been proposed.

15 Sn-Ag-Bi and Sn-Ag-Cu-Bi alloy compositions are well documented as lead-free solder alloys. The concept of combining high and low melting point alloy powders to form a mixture which melts at a low
20 temperature but forms a high melting point joint is also well documented. However, the use of such alloys with a melting range to inhibit tombstoning is not known, and has not been documented.

25 We have found that solder pastes made with mixtures of Sn63Pb37 powder and Sn62Pb36Ag2 powder, melting at 183°C and 179°C respectively surprisingly give a significantly reduced tendency to tombstoning as compared to pastes made up with prealloyed powders,
30 when used to solder chip components on printed circuit boards.

 On this basis we have concluded that use of a mixture of a SnBi alloy powder, such as a Sn43Bi57
35 powder, and a SnAgCu alloy powder, such as Sn96.5Ag3.8Cu0.7 powder, such specific alloys melting

at 138°C and 217°C respectively, in a (lead-free) paste, will analogously also have an anti-tombstoning effect as well as enable the paste to start to reflow at a lower temperature than if prealloyed powder were used.

According to one aspect of the present invention, there is provided a method of securing a chip component to a printed circuit board and, in so doing, achieving the combined effects of reducing tombstoning and reducing solder paste reflow temperature, which comprises carrying out soldering with a paste of a first solder alloy powder to which is added a powdered lower melting alloy which melts at a lower temperature than said first solder alloy and which, when admixed with the paste of the first solder alloy, forms a higher melting point joint than that attainable with only the paste of the second solder alloy.

In a second aspect, this invention provides a method of reducing susceptibility to tombstoning and reducing the melting point of a lead-free solder alloy in a solder paste being used to attach chip component to a printed circuit board, which comprises adding to a paste of a first solder alloy powder, which paste is a lead-free solder paste, a SnBi alloy powder, which is lower melting than the first solder alloy powder, to produce a bismuth containing final alloy containing from 1-10% bismuth, the first solder alloy containing 0-5% Cu, 0-10% Ag and 0-5% Sb, the remainder being Sn and at least one of Cu, Ag and Sb being present in a minimum amount of 0.1%.

All percentages expressed herein are on a weight basis.

5 Addition of SnBi powder addition to a lead-free solder paste, in particular SnAgCu solder paste is particularly noteworthy in that the paste starts to reflow at a lower temperature, reducing the required peak reflow temperature.

10 We have further found that the reduction in tombstoning is enhanced if the lower melting alloy is present as a finer size powder than the higher melting alloy which is present as a larger size powder. Preferably, the lower melting point alloy is employed in the form of a powder of which the particle size is predominantly less than 25 μm diameter, while the first solder alloy powder particle size is predominantly greater than 25 μm diameter. More preferably, the lower melting point alloy particle size is predominantly in the range 10-25 μm and the first solder alloy particle size is predominantly 20-45 μm . By the word predominately, it is meant that more than 50% by wt., preferably more than 75% and most preferably all of the alloy in question has the indicated particle size. It is hypothesised that the fine lower melting powder particles melt first and form a network of liquid around the larger powder particles. This liquid network enables wetting to take place more readily and initiate reflow, and maximises the effective melting range to minimise tombstoning.

30 In preferred practice, there is used a starting alloy containing up to 3% Cu, up to 5% Ag, and up to 5% Sb, the remainder being Sn and at least one of the elements Cu, Ag and Sb being present in an amount of at least 0.1%.

35 It is found typically in the practice of this invention that, when using a starting alloy of SnAg3.8,

Cu0.7 in the form of a solder paste to which Sn43Bi57 is added in powder form in an amount to give an alloy having an overall content of 5% Bi, as a result of the SnBi alloy powder addition, the reflow temperature
5 needed is reduced by about 10°C. This is noticeably greater than the 2°C reduction in liquidus temperature expected with 5% Bi addition to a SnAgCu eutectic. It is considered that this enhanced behaviour results from adding the bismuth as a powder concentrate to the other
10 components already in alloy form, instead of using a homogeneous alloy, in that latent heat of melting is absorbed over a greater temperature range, starting at 138°C, the melting point of the SnBi eutectic, thereby reducing temperature lag between PCB and solder joint
15 and allowing a lower reflow peak temperature than is achieved when using the equivalent homogeneous alloy, paste containing Bi.

A further advantage of the use of SnBi as powder admixture stems from the fact that, in solder pastes, the oxide content of the powder needs to be as low as possible, to give good reflow. Adding bismuth to a high tin or tin-lead solder in conventional manner changes the oxide formed on the powder surface from tin
20 oxide to mixed oxide containing bismuth as well as tin. The mixed oxide grows faster than the tin oxide, so bismuth alloy solder powders contain more oxide than non-bismuth alloy solders, and deteriorate faster in storage. Making the alloy using a powder and mixture
25 will give a lower overall oxide content, hence better storage and reflow properties.

It has already been stated herein that the final alloy should have a Bi content of 1-10% this amount
35 preferably being in the range from 2-6% and most preferably being about 5%. Up to 1% of Ag, Cu and Sb

can each be employed in the bismuth containing additive alloy which preferably contains 40-70% Bi and the remainder tin. Because of these two factors, if one or more of Ag, Cu and Sb is to be present, preferably care should be taken to have the final alloy show the following analysis:-

	Ag	up to 6%
	Cu	up to 3%
10	Sb	up to 5%
	Bi	1-10%
	Sn	rest

CLAIMS

1. A method of securing a chip component to a printed circuit board and, in so doing, achieving the combined effects of reducing tombstoning and reducing solder paste reflow temperature, which comprises carrying out soldering with a paste of a first solder alloy powder to which is added a powdered lower melting alloy which melts at a lower temperature than said first solder alloy and which, when admixed with the paste of the first solder alloy, forms a higher melting point joint than that attainable with only the paste of the second solder alloy.
2. A method of reducing susceptibility to tombstoning and reducing the melting point of a lead-free solder alloy in a solder paste being used to attach chip component to a printed circuit board, which comprises adding to a paste of a first solder alloy powder, which paste is a lead-free solder paste, a SnBi alloy powder, which is lower melting than the first solder alloy powder, to produce a bismuth containing final alloy containing from 1-10% bismuth, the first solder alloy containing 0-5% Cu, 0-10% Ag and 0-5% Sb, the remainder being Sn and at least one of Cu, Ag and Sb being present in a minimum amount of 0.1%.
3. A method as claimed in Claim 2, wherein the first solder alloy powder contains from 0.1-3% Cu, from 0.1-5% Ag and from 0.1-5% Sb.
4. A method as claimed in Claim 2, wherein the first solder alloy powder has the composition $\text{SnAg}_{3.8}\text{Cu}_{0.7}$.

5. A method as claimed in any preceding claim,
wherein the final alloy has a Bi content in the
range from 2-6%.
- 5 6. A method as claimed in any one of Claims 2 to 3,
wherein the SnBi alloy powder contains from 40-70%
Bi.
- 10 7. A method as claimed in Claim 7, wherein the SnBi
alloy powder additionally contains one of more of
Ag, Cu and Sb.
- 15 8. A method as claimed in any one of Claims 2-8,
wherein the final alloy has an analysis:-
- | | |
|-------|----------|
| Ag | up to 6% |
| Cu | up to 3% |
| Sb | up to 5% |
| Bi | 1-10% |
| 20 Sn | rest |
9. A method as claimed in any preceding claim which
is applied to the production of a solder pad
affixing a component to the surface of a conductor
on a dielectric substrate.
- 25 10. A method as claimed on any one of claims 1-9,
wherein the lower melting point alloy is employed
in the form of a powder of which the particle size
is predominately less than 25 μ m diameter, while
30 the first solder alloy powder particle size is
predominately greater than 25 μ m diameter.